

# Laser Scattering Particle Size Distribution Analyses of Pigments

by Philip Patterson and William Lum

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#### **Abstract**

The degree of pigment dispersion determines the coating's characteristics and performance. Through the use of the laser scattering particle size analyzer, measurements of particle size distribution range define the actual state of dispersion and, eventually, the characterization of military coating materials and other paint products. Standard materials (e.g., latex spheres of different particle sizes) were chosen to validate the operation of the instrument and to cover the wide dynamic range of the instrument's measurement and capability. Post-validation runs were made on several coating materials, including a polydispersed paint conforming to the U.S. Department of the Army military specification MIL-C-53039A, "Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant." This report details the instrumental parameters and sample preparation procedures used for the determinations. Additionally, the results of analysis are graphically displayed and discussed. A brief description of merited future work is also provided.

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### 1. Introduction

An important step in the processing of protective coatings is the dispersion of the pigment particles within the resinous component of the system. When formulating these coatings, the pigment is usually dispersed in a portion of the vehicle (composed of the binder and solvent) by means of a high-speed mixer or mill. After milling, the homogenity of pigment incorporation is oftentimes evaluated by measuring particle agglomerates. Excess particle agglomeration can have detrimental effects on the appearance, as well as the optical and rheological properties of the final paint product.

A method for measuring these oversized particles involves the use of a fineness of grind gauge. The test for determining fineness of grind, or degree of dispersion, is performed by spreading a portion of the coating along a calibrated, depth-tapered path. At some point along this path, oversized particles or agglomerates will become visible. A numerical value in Hegman scale or micron units is taken from the calibrated scale at the point where the particles form a definite pattern. The American Society for Testing and Materials (ASTM) (1996) Method D-1210-79 (reapproved 1988) "Standard Test Method for Fineness of Dispersion of Pigment - Vehicle Systems" is a commonly referenced procedure for this type of evaluation. And although the test is simple and inexpensive to perform, it is somewhat limited in scope. The technique is nonquantitative and gives, at best, only an indication of particles whose dimensions are about  $10~\mu$  or greater. Since many of the prime pigments used in the U.S. Army's camouflage topcoats are less than  $10~\mu$ , the grind gauge cannot accurately detect all of these sized particles.

Additionally, a single value is generated using a grind gauge for a given coating formulation. However, since pigments of various dimensions exist within the coating matrix, a measurement involving a particle size distribution range would more thoroughly define the actual state of dispersion. This study involves the use of such a measurement device, the classical angular laser scattering particle size analyzer. This instrument will be used to perform particle size distribution analysis for the characterization of military coating materials and paint products.

## 2. Approach

The instrument that was used for authors' preliminary analyses was the Horiba Model LA-900 laser scattering particle size distribution analyzer (Horiba Instruments Incorporated, Irvine, CA) (Figure 1). Based on Gustave Mie scattering theory of measurement, particles suspended in a liquid as small as  $0.04~\mu m$  can be determined. The LA-900 instrument takes advantage of this theory by using front, side, and rear scatter detectors. Then, the Mie theory is drawn upon to calculate the particle size distribution of a given sample. Measurement is possible on the Horiba LA-900 over a wide range from  $0.04~\mu m$  to  $1,000~\mu m$ , which is a huge advantage over the grind gauge or even the coarse particle sieve.



Figure 1. Horiba Model LA-900 Laser Scattering Particle Size Distribution Analyzer.

A fraction cell with a magnetic stirrer in a cell holder was the sampling option selected for use over a circulation cell or flow cell. This allows the measurement of minute quantities of a sample without loss of the sample material. Also, the rapid deterioration of seals and tubing due to the kinds of particles and dispersants used is a major drawback, if circulating techniques are chosen.

Standard materials, such as monodispersed polystyrene latex spheres from Duke Scientific Corporation, Palo Alto, CA, were chosen to validate the operation of the instrument. These materials are used for total performance testing of the entire system's operation and should produce very narrow distribution results.

The software that generated the graphics display and performed the instrument control and data calculation was the Horiba LA-900 Measure Version 2.00d and the Horiba LA-900 Refraction Indices Version 2.00d. The software and operation are interfaced with Microsoft Windows operating system Version 3.0. All program software was loaded on a Compaq Prolinea 486/33-mHz desktop computer. Normal measurement time is approximately 30 s per run.

## 3. Experimental

Standard materials from Duke Scientific Corporation were procured at different particle sizes to cover the wide range of measurement and the instrument's capability. The recommended series of size standards are 102 nm, 503 nm, 0.993  $\mu$ m, 9.975  $\mu$ m, and 100  $\mu$ m. This phase is a critical preliminary step in which the standard runs validate the instrument's condition and operation, as well as assure the proper setup procedures when using a fraction cell.

Duke Scientific products are packaged as aqueous suspensions in dropper-tipped vials. Three or four drops of the standard suspension in a deionized (DI)-water-filled fraction cell will place it at the right concentration or loading for measurement.

The conditions were given by Duke Scientific to run standards as follows: set the relative refractive index at 1.19–9.99i and the form of distribution at 3. These instrument settings are recommended when analyzing nearly ideal samples. That is, when the particles are small, spherical, and transparent and have a very narrow range of distribution. Also of note, only DI water was used as the dispersing fluid or dispersant. No surfactants (cationic, anionic, or nonionic) were added to the standard solutions.

When the authors were satisfied with the standard runs' results, particle size determinations were made on titanium dioxide (TiO<sub>2</sub>) pigment, a major component in most chemical agent resistant coating (CARC) primer and desert-colored paints. A TiO<sub>2</sub> hand-mixed slurry was dispersed by using DuPont Pigments and Dispersions, Inc., Wilmington, DE, Ti-Pure R960 in Reichhold Chemical Products Company, Pittsburgh, PA, no. 6440 alkyd resin (1:1 ratio) with methyl ethyl ketone and methyl (MEK) iso-butyl ketone solvent system (1:1:1/2:1/10 ratio, respectively).

The next logical step was to analyze a typical "wet" paint sample. A polyurethane topcoat conforming to the military coating specification MIL-C-53039A "Coating, Aliphatic Polyurethane, Single Component, Chemical Agent Resistant," (U.S. Department of the Army 1989) was selected for the trial runs. These coating analyses were not made to yield absolute particle size determinations, but rather to give the analysts an idea of the type of data that could be obtained, as well as to develop a reliable sampling technique when dealing with viscous materials. The samples were prepared by an initial dilution with MEK in a given ratio of 0.5:1. After thorough mixing, additional MEK was added to optimize the concentration level. This level is readily verified by placing the diluted sample into the instrument's light path and checking the degree of transmittance (about 80–90% T). This dilution process also worked well when preparing and analyzing other coating materials, such as carbazole violet, a minor but very important camouflage tinting pigment found in several Green 383 CARC formulations.

#### 4. Results

Figure 2 represents an initial validation run using polystyrene microspheres. The particle size standard (lot no. 18267) was certified to have a mean diameter of 0.993  $\mu m \pm 0.021 \ \mu m$  with a standard deviation of 0.010  $\mu m$  and a coefficient of variation equal to 1.0%. Measurements were made via surface analyzer techniques. As shown, the results obtained from the LA-900 laser scattering particle size analyzer are consistent with the size limits set forth by the supplier  $\pm$  10% error and < 5% spread range, respectively.

Figure 2. Validation Run at Fort Belvoir, VA (Before Move) Standard. From Duke Scientific Corporation, Palo Alto, CA, Polymer Microspheres Lot No. 18267 0.993  $\mu$ m  $\pm$  0.021  $\mu$ m.

Figure 3 represents an additional validation run on another microsphere standard (lot no. 18401) having a mean diameter of  $9.975~\mu m \pm 0.061~\mu m$ . As before, the analyzed median diameter of  $10.48~\mu m$  is within the expected size and spread range limitations. Noteworthy is that these analyses were performed in two different laboratories. The initial validation run (Figure 2) was performed at the Communications and Electronics Command's (CECOM) Research, Development, and Engineering Center located at Fort Belvoir, VA. The Figure 3 analysis was performed at the U.S. Army Research Laboratory (ARL) (Bldg. 4600), Aberdeen Proving Ground (APG), MD. The dual-location analyses were a result of a mission transfer due to the Base Realignment and Closure Act (BRAC). The quality of the validation data obtained indicated that the instrument's condition was not adversely affected during the relocation process between laboratories.

Figure 4 represents the particle size analysis of the  $TiO_2$  pigment sample, dispersed as previously discussed. As shown, the median particle diameter was measured at 0.48  $\mu$ m. This is in close agreement, within 5%, of the manufacturer's reported value of 0.50  $\mu$ m. It should be noted that the manufacturer's technique for measuring particle size was light microscopy. The analyst should be aware that each measurement technique detects size through its own physical principle and that no single instrument can provide a universal answer.

Figure 5 represents the particle size distribution analysis of the selected whole paint. This tan-colored solvent-based coating contains pigment particles of various sizes, shapes, and chemical compositions. Upon inspection, the graph quite clearly shows a well-resolved multimodal distribution with particle sizes ranging from approximately  $0.1~\mu m$  to  $50~\mu m$ . And although the shape of the graph does indeed represent a polydispersed system, the actual diameter values must be considered with care since the conversion algorithm or mathematical function used for the light scattering has not been thoroughly reviewed for bias.

#### 5. Conclusion

Laser-light scattering shows promise as a reliable method when performing particle size analysis on coatings and related materials. A wide dynamic range  $(0.1-1,000 \mu m)$  of particle sizes can be

Figure 3. Validation Run After Move (APG Site) Standard. From Duke Scientific Corporation, Palo Alto, CA, Polymer Microspheres Lot No. 118401 9.975  $\mu$ m  $\pm$  0.61  $\mu$ m.

Figure 4. Particle Size Analysis of a TiO<sub>2</sub> Sample.

Figure 5. Particle Size Analysis of a CARC Paint.

determined in a single measurement on a variety of coating products and raw materials. Measurement times are fast (typically 20–40 s), allowing for the possibility of a high-volume sample turnaround capability. Instrument operation can be quickly learned, the software is user-friendly, and checking the system's performance is easily verified by using routine control materials. Small and/or hazardous samples can be analyzed with the use of a fraction cell.

As with any new laboratory technique, the analyst should be aware of the limitations of the instrument's capability. Errors in size distribution results obtained from light scattering measurements primarily involve the optical arrangement of the instrument's multidetector and the matrix conversion (especially, the complex optical correction model) algorithm or mathematical function chosen by the user during data retrival.

#### 6. Future Work

Particle size analysis will continue using the static laser-light scattering technique with the focus on camouflage coating samples and their relative degree of pigment dispersion. Special attention will be given to which optical model is best suited for converting the light scattering data into the corresponding size distribution. For a given analysis, an improper optical model selection can be monitored by observing the resulting distribution graph for (1) multiple artificial peaks, (2) excessive peak broadening, and/or (3) incorrect reporting of median, mean, and mode particle size data.

Further, since the light scattering measurements are based on the optical properties of the particle, a greater emphasis will be placed on choosing the sample's relative refractive index value, as well as its imaginary factor value. The selection of the proper value is a vital key in obtaining accurate size distribution for a given dispersion.

Also of interest is the evaluation of particle size determinations when coupled with data obtained from other coating characterization techniques, such as film surface imaging and profiling.

## 7. References

- American Society for Testing and Materials. "Standard Test Method for Fineness of Dispersion of Pigment Vehicle Systems." ASTM D1210-79, 1996 Annual Book of Standards, vol. 06.01, pp. 106-113, 1996.
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